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Research paper

Ultrasound velocities and elastic properties of LICL doped zinc –borate glasses

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Abstract

Sound velocities and elastic property measurements have been employed to study the strength and rigidity of the structure of ZnO-B2O3 glasses doped with LiCl. Moduli of elasticity such as longitudinal, Young`s , bulk and shear modulus have been calculated using ultra sound velocities such as longitudinal and transverse velocities are measured at a frequency of 10 MHz as function of LiCl concentration. Both sound velocities and elastic moduli decrease with increase of LiCl concentration. The results are discussed in the view of borate network and dual structural role played by the divalent zinc ions present in the network. The results indicate that the Zn+2 ions are likely to occupy network forming positions in this glass system. While LiCl is a typically dissolved in the borate network and Cl- occupy the interstitial positions.

Keywords: *Elastic Properties; Ultrasound Velocity; Poisson's Ratio.*

1. Introduction

Alkali modified glasses have been extensively studied in the recent years to elucidate the nature and the relative concentration of the various borate units (Meta, pyro- and ortho-borates) constituting the glass network. The ability of boron to exist in [3]-and 4-coordinated environments and the high strengths of covalent B-O bonds enable borates to form stable glasses. The 11BNMR investigation [1,2] and the IR investigations [3] were important in identifying various borate species consisting of borate –oxygen trian- gles and tetrahedra which forms the glass network at various modification levels. Alkali modified borate glasses containing divalent oxides as ZnO, BaO, PbO, MgO, CuO, exhibit an inter- esting behaviour in the glass network structural and NMR studies on Li2o-PbO-B2O3 and Na2O-MgO-B2O3 ZnO-B2O3-V2O5 [4]
PbO-B2O3-V2O5 [5] PbO-Na2B4O7 [6] glasses it is shown that the divalent ions Pb2+ and Mg2+ are in network forming and network modifying positions [7]. The pressure dependence studies of Na+ ion of electrical conductivity on Na2O-ZnO-B2O3 glasses has also been studied and the results indicate that the Zn2+ ions
Prefer network-forming positions. Damodaran et al [8] reported
The dual role of divalent ions is not ony seen in borate glasses but also in silicate sand phosphomolybdate glasses.
Among the various experimental techniques available for studying structure –property relations operating in solid materials elastic properties play a considerable significance. Since the measurement yield information concerning the forces operating between the atoms or ions comprising solid, is fundamentally important in in- terpreting and understanding the nature of bonding in the solid state. Therefore the choice of the appropriate material for particular application requires knowledge of its physical band mechanical properties. Hence mechan- ical properties are suitable for describing the glass structure as a function of composition. I have reported studies on several binary alkali borate glasses and estab- lished a correlation between elastic properties and borate glass structure. In Na2O –B2O3 glass system the elastic properties of Na2O-B2O3 glass system view of boron coordination. Elastic properties of various borate glasses have been reported by Pakade et al 1992 [9], in this
work we attempted to examine the role of Zn2+ ion in LiCl -B O glass system using elastic properties .

2. Experimental

Glasses were prepared by the standard melt quenching method using the general formula xLiCl-(100-X)[0.40 ZnO:0.60 B2O3] where 5≤ X ≤30.The starting materials were mixed well by grinding ion appropriate quantities to constitute 12 gm batch. The ground mixtures were heated in a silica crucible. The temperature of the furnace fixed at 623K for about 2 hours to decompose 2H3BO3 to B2O3.H2O the batches were then melted at 123K for about 10 minutes-to get a homogeneous pre –heated brass blocks. The cylindrical shaped samples were obtained for ultrasonic measurements by quenching the melt in a brass mould which was pre heated (about 2000C) to avoid breaking of the samples due to thermal strains .All the samples were annealed below the transi- tion temperature. The glasses were checked by X-ray diffractome- ter (model Rigaku DMAX-1C) by employing Cr-Kα radiation. The X-ray diffactogram did not show any sharp peaks, a characteristic of amorphous nature. The density of glass samples were measured of by Archimede`s principleusing toluene as immersion liquid (density =0.86gm/cm3) Molar volume has been calculated from the molecular weight M and density (ρ) of the samples using the rela- tion Mv= $\frac{M}{\rho}$. For elastic measurements, sample were polished using a lapping tool to get a uniform parallel surfaces of the samples were achieved. Ultrasonic velocity measurements were carried oput at frequency of 10 MHz using X-cut , Y-cut quartz transduc- ers. A pulse superposition technique has been employed using Ultrasonic interferometer (system Dimensions, Bangalore) sal- ol(phenyl salicilate) has been used as a bonding material between the glass samples and transducers. Using Mckskimin`s Δt criteria the round trip delay time τ have been calculated (Mckskimin`s 1961,Meskimin et al 1962). By measuring the thickness of a sam- ple (d) longitudinal (Vl) and transverse (Vt) wave velocities were calculated using the relation $V = \frac{2d}{t_0}$ m/sThe various elastic properties of the glasses were calculated using the following relations

Longitudinal modulus L = ρV 2 (1)

Shear modulus

G = ρVt2 (2)

Bulk modulus

$K = L - \frac{4}{3}G$ (3)

Young`s modulus E = (1+2σ) 2G (4)

Poisson's ratio

$\sigma = \frac{L-2G}{2(L-G)}$ (5)

where L, G, K and E are longitudinal, shear, bulk, and young`s modulus respectively. P is the density, σ is the Poisson's ratio, (Vl) and (Vt) longitudinal and transverse sound velocities re- spectively.

3. Results and discussion

The variation of density and molar volume of LB glass series is shown in figure 1. It can be seen from the figure 1 that the density decreases monotonically while the molar volume increases with the increase of LiCl concentration. The variation of density with LiCl concentration can be explained by considering the structural changes occurring due to the isotropic dissolution of LiCl in the modified boron glass network. The structure of crystalline as well as amorphous B2O3 is made up planar [BO3/2]0 triangles [10].

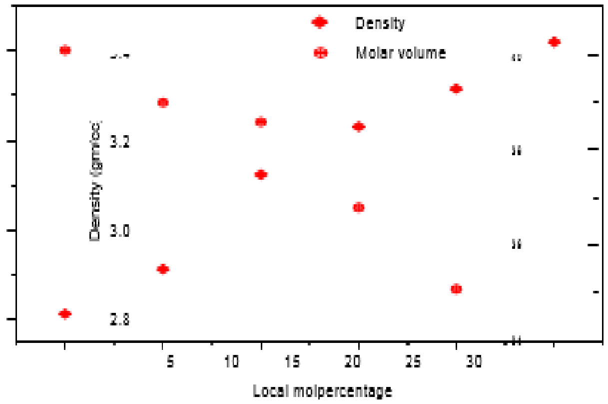

Fig. 1: Variation of Density and Molar Volume with Licl Mol Percentage.

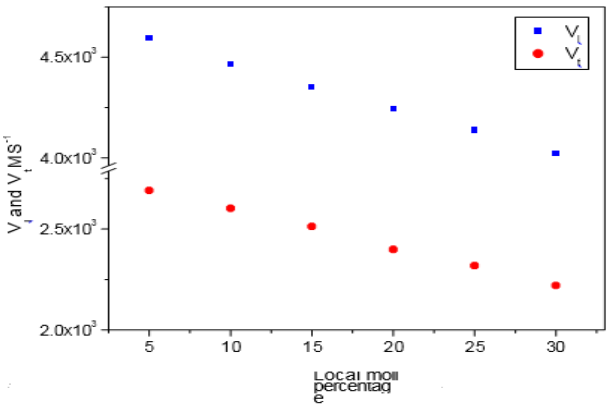

Fig. 2: Variations- of VL and VT with LICL Moll Percentage.

In amorphous B2O3, most of these triangles are arranged into boroxyl rings in which three oxygens are part of the ring and three oxygens are outside the ring. These rings are randomly interconnected through loose [BO3/2]0 units. Due to the addition of modifying alkali oxide such as ZnO the three coordinated triangle [BO3/2]0 units are converted to four coordinated boron tetrahedra [BO4/2]0 and thus the network dimensionally and connectivity increases. Cl- ions enters the B2O3 glass network interstitially by increasing the volume of the structure. This is also reflected in the variation of molar volume versus LiCl concentarion.

3.1. Sound velocities

The elastic moduli are proportional to the square of velocity, a plot of sound velocities versus LiCl mol% is indicative of relative structure. The compositional dependence of longitudinal and transverse sound velocities is shown in the figure 2. Figure 3 shows the variation of elastic moduli as a function of LiCl concen- tration's can be seen from the figure 2&3 that both Vl , Vt and elastic moduli decrease with the increase of LiCl concentration over the entire composition studied.

This variation of sound velocities and elastic moduli can be explained on the basis of the structural consideration of borate network. As pointed out in the earlier section that vitreous B2O3 consists of planar [BO3/2]0 triangles. The addition of ZnO to B2O3 network creates [BO4/2]- units. This leads to increase in the network dimensionality and connectivity. Hence, both velocities and elastic moduli decrease with decreasing ZnO concentration. It may also be noted from the figure 3 that the rate of change of elastic moduli is more pronounced in L and least in case of G. This indicates resistance to the deformation and it is most probably due to the presence of less number of covalent bonds.

It is well known fact that in borate glasses, addition of ZnO to B2O3 network creates [BO4/2]- units up to 33.3 mol% of modify- ing oxide, Further addition of modifying oxide leads to reconver- sion of [BO4/2]- to [BO3/2]- units [10] this leads to loose struc- ture because of the presence of non-bridging oxygens (NBOs) .In the present glass system if Zno were to be incorporated into the network as aglass modifier, one would have expected non-linear

Variation in both velocities and elastic moduli when the effective concentration of modifier oxide exceeds to 33.3molpercentage. It can be Noted that ZnO concentration increases from 28 to 34 when LiCl content varied from the 30-molpercentage to 15-mol%. Further decrease in LiCl content results in the enhancement in ZnO content from the 33.3mol%.Hence it is expected a nonlinear variation if ZnO play a modifying role. But the

Observed variations in sound velocities and elastic moduli show only linear variations .This suggest that ZnO is interpreted into the borate network as galas former.

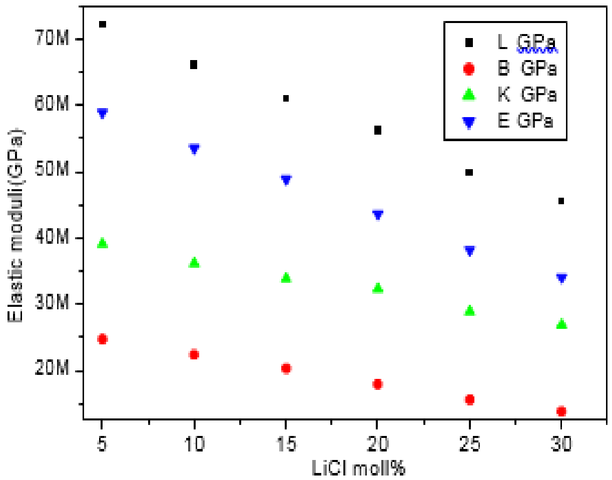

Fig. 3: Variation of Elastic Moduli with LICL Molpercentage.

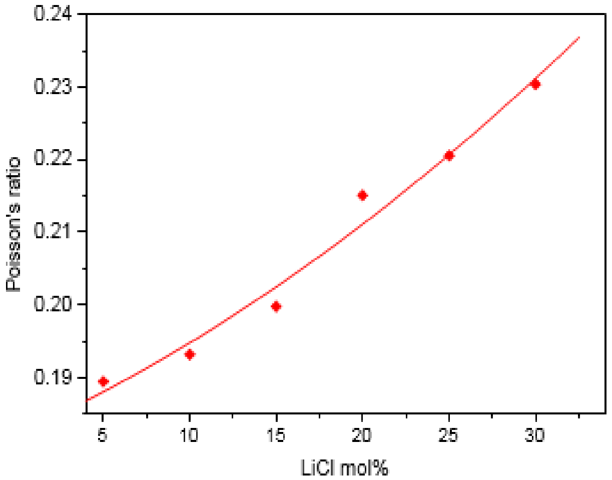

Fig. 4: Variation of Poison’s Ratio with LICL Mol percentage.

3.2. Poisson`s ratio

The compositional dependence of Poisson`s ratio as a function of LiCl concentration is shown in figure 4. Poisson`s ratio of the transverse and linear strains for a linear stress. It has also been discussed in terms of the dimensionality of the glass network and it is observed that the Poisson’s ratio for a three dimensional net- work is less than that of two-dimensional structure, which in turn is less than that of a one-dimensional structure.

This has been attributed due to the fact that as the concentration of bonds resisting a transverse deformation decreases in that order [8].As it can be seen from fig 4 that the Poisson`s ratio is found to be increase even when the effective concentration of modifier is greater than 33.3mol%.This again suggest that there is no formation [BO3/2] - groups with NBO`s. Further, the values of poison’s ratio are that of covalently bonded structure. Compactness in the structure leading to increase in mean sound velocity [8]. The above observation based on the elastic properties and Poisson’s ratio indicates that Zn+2 ions prefer network forming position at high concentrations. Further the decrease in the Ultra sound veloc- ities and elastic moduli can be attributed to the decrease in con- centration of the NBO`s.

4. Conclusions

Elastic property studies on LiCl – ZnO –B2O3 glasses have been carried out as a function of lithium chloride concentration. The variation seen in ultrasound velocities and elastic moduli are relat- ed to volume increasing effect caused due to the isotropic dissolu- tion of LiCl in the macromolecular structure formed by ZnO-B2O3.

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